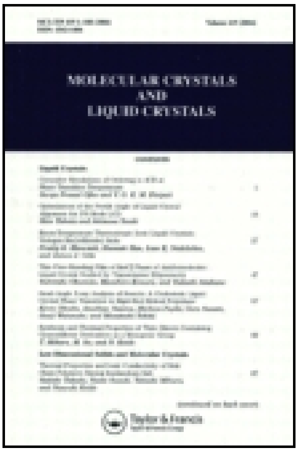

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Effect of Elemental Substitution on the Superconductive Properties in $Bi_2Sr_2Ca_{n-1}Cu_nO_y$

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EFFECT OF ELEMENTAL SUBSTITUTION ON THE SUPERCONDUCTIVE PROPERTIES IN $Bi_2Sr_2Ca_{n-1}Cu_nO_y$

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Abstract Effects of Pb substitution and N_2 annealing on the superconductivity of $Bi_{2-2x}Pb_{2x}Sr_2Ca_{n-1}Cu_nO_y$ have been studied. Hole concentration of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (n=2,3) was controlled by the substitution of Pb for Bi. The Tc dependence on the hole concentration in n=3 was different from that in n=2. The optimum hole concentration for highest Tc in n=3 phase was larger than that in n=2 phase. By annealing the n=2 phase in N_2, $Bi_{2-2x}Pb_{2x}Sr_2CaCu_2O_y$ with $0.2 \le x \le 0.3$ became monoclinic. The Tc of this monoclinic $Bi_{2-2x}Pb_{2x}Sr_2CaCu_2O_y$ was observed above 97.5K.

INTRODUCTION

Tc's of cuprate superconductors are very sensitive to their hole concentration (C_{hole})[1]. Recently, Fukushima et al.[3] have reported that Pb substitution for Bi in $Bi_{2-2x}Pb_{2x}Sr_2Ca_{n-1}Cu_nO_y$ removes oxygen from the system with C_{hole} unchanged. On the contrary, some groups have revealed that Pb substitution produces a hole to n=2 phase[2,4]. This discrepancy may be caused by the difference of the sintering condition particularly of partial O_2 pressure.

In this paper, Pb substitution effect on Tc was studied in n=2 and 3 phases. Especially for the n=2 phase prepared under various O_2 pressure, changes in the structure and the Tc dependence on Pb content was examined. It was found that 1) by sintering in 1/18 O_2, substitution of Pb for Bi produces a hole, 2) the optimum C_{hole} per a unit cell for the maximum Tc in n=3 phase is larger than that in n=2 phase and that 3) Pb substitution or low oxygen pressure annealing promotes the structure change from pseudotetragonal into orthorhombic and for the Pb substituted ($x \geq 0.2$) system, N_2 annealing procedure leads the changes of the orthorhombic into the monoclinic structure. Maximum Tc observed for the monoclinic n=2 phase was above 97.5K.

EXPERIMENTAL

Samples were prepared by dissolving nitrates in water, followed by evaporation and calcination in air at 800℃ for 2 hours. This powder was then reground, pressed into pellets, sintered in 1/18-1/5 atmosphere of O_2 for 40-60 hours at 800℃. They were post annealed in N_2 at 750℃ for 8 hours. Four kinds of samples with different composition were synthesized, whose nominal ratios of Pb/Bi+Pb were (a)0, (b)0.05, (c)0.20 (d)0.30 and (e)0.50.

EPMA was carried out using AN 10/85S system by Link Analytical Co. attached to SEM (JSM-840A, JEOL) in order to determine the composition of the superconductor.

The structure of the compounds were determined by X-ray powder diffraction patterns using CuKα (RAD-IIIB, Rigaku denki). The peaks were assigned according to those indexed by M.Onoda et al[9]. Superconductive property was measured by the temperature dependence of both resistance and ac magnetic susceptibility. Resistivity measurements were carried out by a standard dc four probe method. Each sample was reground and pelletized prior to the ac susceptibility measurements. Tc was determined by the onset of as susceptibility.

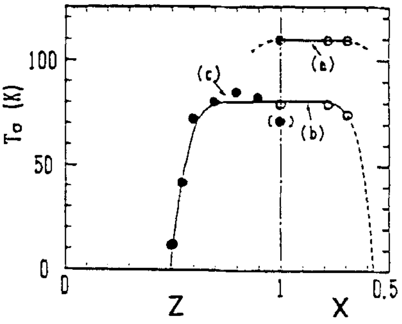

FIGURE 1 Tc dependence on C_{hole} in $Bi_{2-2x}Pb_{2x}Sr_2Ca_{n(1-z)}Y_{nz}Cu_nO_y$

a)hole doping by Pb substitution in n=3 phase

b)hole doping by Pb substitution in n=2 phase

c)hole quenching by Y substitution in n=2 phase[1]

RESULTS AND DISCUSSION

Tc dependence on the hole concentration

As shown in Figure 1, Tc of n=2 phase decreased to 74.5K in x=0.31. This is due to the overdope of holes[2,4] by Pb^{2+} substitution for Bi^{3+}. In n=3 phase, Tc dependence on C_{hole} was much smaller than that in n=2 phase. This suggests that the optimum C_{hole} for the highest Tc in n=3 phase is larger than that in n=2 phase. Further problem whether the optimum hole concentration per a Cu atom to give maximum Tc is different in n=2 and 3 has to be solved. It is necessary to measure how much holes are located in pyramidal and planar Cu-O layers in n=3 phase.

N_2 annealing effect

As shown in (a) and (b) of FIGURE 2, the structure of $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_y$ changed drastically with reducing oxygen pressure. Reduction of oxygen pressure from 1/5 to 1/13 leads to the split of (2000,0200), which means that pseudotetragonal phase changed into orthorhombic[3]. By annealing sample (a) in N_2 at 750°C for 20 hours, (1130,1150,1170) peaks broadened as shown in (c). In particular, split of the peak was confirmed in (1170). This behavior cannot be explained by pseudotetragonal nor orthorhombic and by monoclinic structure. The peaks were indexed with monoclinic structure in a=5.428A, b=5.358A, c=30.77A and γ =90.8° . The peaks agreed well with calculated ones.

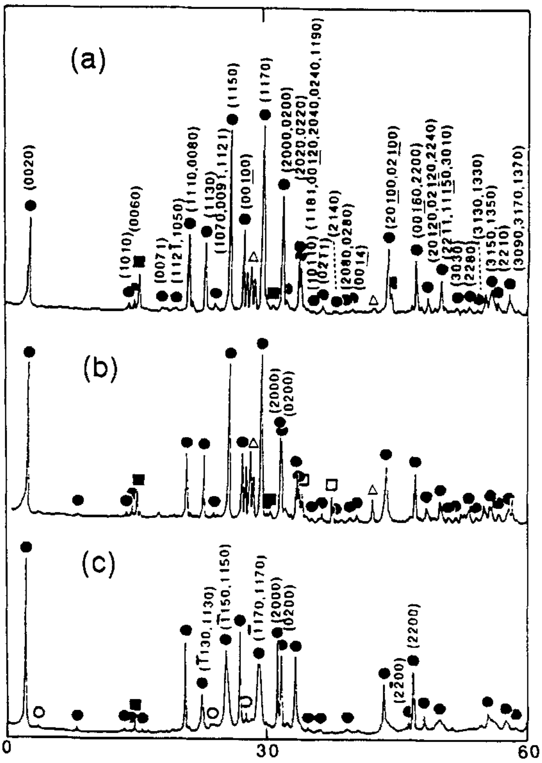

FIGURE 2 XRD patterns of $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_y$

(a)annealed in 1/5 O_2
(b)annealed in 1/13 O_2
(c)annealed in 1/5 O_2 followed by N_2

●:n=2 phase ○:n=1 phase ■:Ca PbO
□:CuO △:unknown phase

As shown in FIGURE 3, monoclinic n=2 phase was prepared only by annealing in low oxygen pressure below 1/18 atm. with Pb of $0.2 \le x \le 0.3$. The c-axes length of monoclinic phases were 30.76-30.77A, which were shorter than that of orthorhombic or pseudotetragonal one (30.79-30.85A). It is reported that removing oxygen from n=2 leads to the increase of c-axis[4], which is mainly considered to be due to the decrease of excess oxygen in Bi-O layer. The opposite behavior for monoclinic phase suggests the change of the structure in Bi-O layer. Another interesting feature is the increase in the intensity of (0020) peak with decreasing oxygen content. More precise analysis is now in progress.

The Tc of monoclinic n=2 phases were 97.5-98.0K as shown in FIGURE 4(a). This temperature was extremely high in comparison with that before N_2 annealing (FIGURE 4(b)). This may be caused by the decrease of hole concentration. The optimum hole concentration to give the maximum Tc in n=2 phase is smaller than that of the

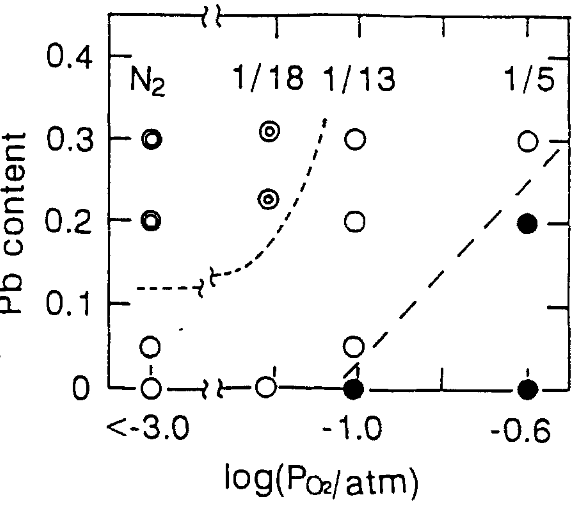

FIGURE 3 Phase diagram of $Bi_{2-2x}Pb_{2x}Sr_2CaCu_2O_y$

◎ : monoclinic
○ : orthorhombic
● : pseudotetragonal

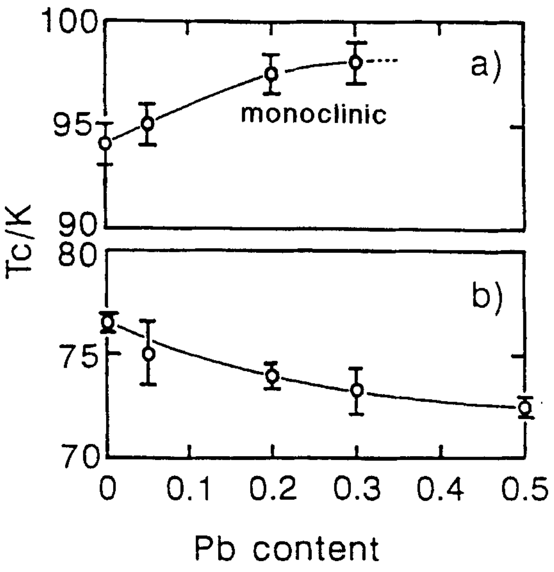

FIGURE 4 Tc dependence on Pb content

(a) after N_2 annealing
(b) before N_2 annealing

sample prepared in air[2,5,6,7,8]. By reducing the system, the value of Tc is expected to increase. Now we are not sure whether the great increase in Tc up to 97.5K can be explained only by the reduction of C_{hole}. Precise measurement on the hole concentration is now in progress.

CONCLUSION

Monoclinic $Bi_{2-2x}Pb_{2x}Sr_2CaCu_2O_y$ with $0.2 \leq X \leq 0.3$ was synthesized by N_2 annealing or by low O_2 pressure annealing. In x=0.2, lattice parameters of a, b, c and γ were 5.428A, 5.358A, 30.77A and 90.8° , respectively. The observed Tc of monoclinic n=2 phase was above 97.5K, which was more than 20K higher than that before N_2 annealing.

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